Table II.

$f = (F-E)/k - \frac{1}{2}kF, \qquad k = \sin\phi.$

ϕ.	f.	ϕ.	f.
0°	0·	55	0·11398
10	0·00049	60	0·1579
15	0·00180	65	0·2172
20	0·00426	70	0·2982
30	0·01515	75	0·4146
35	0·02461	80	0·5932
40	0·03693	85	0·9213
45	0·05647	89	1·7199
50	0·08106	90	∞

A Spectroscopic Investigation of the Ionisation of Argon by Electron Collisions.

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Introduction.

The authors have previously described an investigation of the effects of electron collisions with argon atoms,* in which the production of radiation and of ionisation was looked for, using a delicate electrometer as the detecting instrument. As the result of these experiments, it was found that the value of the minimum electron energy for the production of resonance radiation from argon was 11·5 volts, and the minimum electron energy necessary for the detachment of a single electron from a normal argon atom was 15·1 volts. Since the publication of these results some other investigations of the critical voltages for electrons in argon have been published. Several of these were made using argon as a gas filling for a thermionic valve, but the precise methods of arranging the electric fields, and of carrying out the experiment differed somewhat in different cases. The values of the ionisation voltage deduced by the various observers are not in good agreement. For instance, from experiments with three-electrode valves, Stead and Gossling† concluded that this value is 12·5 volts, Hodgson and Palmer‡ that it is 16·6 volts, and

* F. Horton and A. C. Davies, 'Roy. Soc. Proc.,' A, vol. 97, p. 1 (1920).

† G. Stead and B. S. Gossling, 'Phil. Mag.,' vol. 40, p. 413 (1920).

‡ B. Hodgson and L. S. Palmer, 'Rad. Rev.,' vol. 1, No. 11 (1920).

Déjardin* that it is 15·0 volts. Found,† using a two-electrode tube, obtained the value 15·6 volts, whereas Rentschler,‡ using a three-electrode apparatus, had previously given 17 volts as the ionisation voltage.

In attempting to account for these discordant values it may be mentioned that in the authors' experiments, already referred to, a very marked discontinuous increase of current occurred a few volts higher than the stage at which ionisation was first detected. This increase of current took place at a potential difference which varied over a range of several volts, but which was never below the ionisation voltage. At certain pressures it was accompanied by the appearance of luminosity in the gas. The effect was attributed to the largely increased electron emission from the glowing filament when neutralisation of the space charge of the electrons in its neighbourhood occurred. It seems not improbable that the effect obtained by Rentschler at 17 volts, and interpreted by him as the beginning of ionisation, in reality indicates the stage when neutralisation of the space charge of the emitted electrons takes place. It also seems probable that the very low value (12·5 volts) obtained by Stead and Gossling must have been due to the presence in the apparatus of some impurity which was ionisable by the argon radiation.

In view of the fact that argon can be stimulated so as to give rise to two quite different spectra—the red spectrum and the blue spectrum—and that it has been concluded, in the first place by Stark and Kirschbaum,§ and subsequently by Friedersdorff,‖ from experiments on canal rays in argon, that the emitters of the spectra are respectively singly and multiply charged argon atoms, it was anticipated that an investigation of the minimum electron energies associated with the excitation of lines belonging to the red spectrum, and lines belonging to the blue spectrum, would supply evidence as to the ionisation voltages of argon.

The advantage of the spectroscopic method of testing for ionisation, over the method of collecting positive ions, is that it gives evidence as to the nature of the positive ions produced in any particular case. Thus, although the test for the presence of positive ions can be made more delicate than the spectroscopic test, particularly in the case of the ionisation of the normal atom, and although accurate values of critical points can best be obtained from current-voltage curves, the spectroscopic test provides the more convincing evidence of the exact significance of particular critical points.

* G. Déjardin, 'Comptes Rendus,' vol. 172, p. 1347 (1921).
† C. Found, 'Phys. Rev.,' vol. 16, p. 41 (1920).
‡ H. C. Rentschler, 'Phys. Rev.,' vol. 14, p. 503 (1919).
§ J. Stark and H. Kirschbaum, 'Ann. der Phys.,' vol. 42, p. 255 (1913).
‖ K. Friedersdorff, 'Ann. der Phys.,' vol. 47, p. 737 (1915).

An investigation of the excitation of the spectra of argon by slowly moving electrons has recently been published by Déjardin,* who took a series of photographs of the spectrum of the glow obtained at different voltages in argon at a pressure of 0·1 mm. His results confirmed in general the conclusions of Stark as to the nature of the atoms emitting the different spectra, but observations were not taken at sufficiently close voltage intervals to give very precise information as to the critical electron energies.

A combination of the spectroscopic and current-voltage tests was applied by the authors to the investigation of the ionisation of neon and yielded interesting results, which have been given elsewhere.† A somewhat similar combination of the two methods was therefore employed in the case of argon, the currents between the electrodes being measured simultaneously with the taking of visual spectroscopic observations.

The experiments to be described in the present paper confirm the values 11·5 volts and 15·1 volts previously obtained by the authors as the minimum resonance radiation voltage and the minimum ionisation voltage respectively, for electrons in argon, and they show that the lines of the red spectrum are those which result from recombination of electrons and positive ions after the occurrence of simple ionisation of the argon atoms. In addition, the experiments show that certain of the "blue spectrum" lines are associated with the removal of two electrons from the normal atom, and that the minimum voltage at which they can be produced by single electron impacts is 34 volts. Under conditions which facilitated the further ionisation of already ionised atoms, it was found that the "blue spectrum" lines could be produced by 19 volts collisions, and that, with very intense bombarding electron streams, lines of this spectrum could be excited at still lower voltages, though no other definite limit associated with their excitation was obtained.

Description of Apparatus.

Two forms of apparatus were used in this investigation; one of these is represented diagrammatically in fig. 1. It resembles that used by the authors in their experiments with neon, its main features being that the spectrum of the glow can be observed in a part of the tube where the bombarding electrons suffer no change of velocity except that which results from collisions with gas atoms, and that the form of the apparatus enables it to be placed between the poles of a strong electromagnet, whereby a concentration of the luminosity into a bright column parallel to the slit of the spectroscope can be obtained. The apparatus contains two parallel platinum

* G. Déjardin, 'Comptes Rendus,' vol. 172, p. 1483 (1921).

† F. Horton and A. C. Davies, 'Phil. Mag.,' vol. 41, p. 921 (1921).

filaments, F, F, coated with a mixture of lime and baryta. Only one of these was used at a time. They were situated about 3 mm. above the circular piece of very fine platinum gauze, G. The piece of similar gauze, H, was 1 cm. below this, and it had a cylindrical piece of platinum gauze fixed round its edges, as seen in the figure. The anode A was a circular platinum plate about 1 cm. in diameter. The spectroscope was arranged so as to view the centre of the tube between G and H in a direction at right angles to the plane of the figure, *i.e.*, in the direction of the lengths of the filaments, so that the luminosity had its maximum brightness in line with the vertical plane through the axis of the collimator.

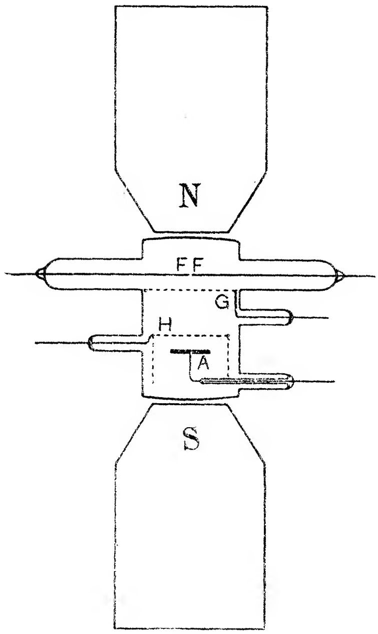

Fig. 1.

The second form of apparatus has already been described in detail by one of us in a paper on the excitation of the spectra of helium.* It was designed mainly for the investigation of low voltage arcs, and consists essentially of a spherical bulb fitted with three tungsten filaments, one of which was used at a time as the source of the bombarding electrons. The anode was a hollow platinum sphere 1 cm. in diameter. The distance of this from the glowing filament could be varied from 1 to 20 mm. The e.m.f. in the circuit was supplied by a 110 volts storage battery, and the potential difference across the discharge tube, and the current through it, could be regulated by means of series and parallel resistances. When a more delicate adjustment of the voltage drop across the tube was required, this was secured by means of a potentiometer arrangement which enabled the potential difference to be varied in steps of one-tenth of a volt.

In order to find the correction which has to be added on to the measured difference of potential between the anode and the glowing filament, so as to give the energy of the electrons in the stream, different arrangements of the electric fields were used in different cases. One of the methods employed with the second form of apparatus, described above, consisted in using one of the cold filaments and its leads as a third electrode, and ascertaining to what negative potential with respect to the negative end of the glowing filament

* A. C. Davies, 'Roy. Soc. Proc.,' A, vol. 100, p. 599 (1922).

this third electrode had to be charged in order to prevent electrons from the filament from reaching it when various potential differences were applied between the hot filament and the anode. This method was used to obtain corrections for ionisation current-voltage curves, and the delicate galvanometer which was employed as the detecting instrument was used at the same sensitiveness as when obtaining the corresponding ionisation current curves. Sometimes the determination of the correction was made using the platinum sphere as the testing third electrode and one of the cold filaments as the anode. It was found that, for any given conditions of pressure and filament temperature, the same value of the correction was obtained by each of the arrangements of electrodes indicated above. Moreover, the value of the correction found in this way was independent of the potential difference applied between the hot filament and the electrode which served as anode, from zero to the first critical voltage. The values of the corrections to be applied in total current curves were determined by finding the value of the negative potential difference which had to be applied between the negative end of the hot filament and the anode, in order to prevent electrons from reaching the anode in sufficient numbers to give an indication on the galvanometer when used at the same sensitiveness as in taking the corresponding total current-voltage curves. All the voltages marked on the curves, and referred to in the following pages, are the values of the electron energies obtained after applying the corrections to the measured potential differences.

The argon used was carefully purified in the manner described in our earlier paper, and the same arrangements were employed for circulating the pure gas through the apparatus. The two forms of discharge tube were connected together, and the argon entered and left through U-tubes immersed in liquid air. Some of the experiments, more particularly those at the higher gas pressures, were carried out with the stopcock between the apparatus and the pump, pressure-gauge, etc., closed. Whenever this communication was opened the U-tube on the pump side of the apparatus was immersed in liquid air.

Before admitting argon to the discharge tubes, the residual gas was removed as completely as possible from the electrodes and glass walls by the method of baking and pumping with a mercury vapour pump, the filaments being maintained glowing during the process. This operation, as usual, occupied several days.

Single Ionisation and the Red Spectrum.

For moderate values of the intensity of the bombarding electron stream, it was found that, as the energy of the electrons was gradually raised, all the

brighter lines of the red spectrum of argon appeared simultaneously, the point at which this occurred being a few volts higher than the ionisation voltage, as indicated by the rise in the ionisation or total current curves. In general, the first visibility of the lines was accompanied by a sudden large increase in the current through the gas, an increase due, no doubt, to the neutralisation of the space charge of the emitted electrons near the filament and the consequent large increase in the electron stream across the tube. After the neutralisation of the space charge had been effected, the voltage across the tube could be reduced considerably without the "red spectrum" lines of argon disappearing, and without there being a discontinuous fall in the current.

For small electron currents the limit to which the lines could be backed was only about 1 volt below the voltage at which they made their appearance, whereas, at the highest filament temperatures, and at moderate gas pressures, the difference between the voltages of appearance and disappearance of the "red spectrum" lines amounted to as much as 11 volts, the lower limit being far below the normal ionising voltage indicated in the curves. Over a considerable range of conditions, however, the limiting voltage for the disappearance of the "red spectrum" lines of argon had a definite fixed value, and a consideration of the current-voltage curves, taken simultaneously with the spectroscopic observations, serves to justify the interpretation of this definite limiting value for the disappearance of lines as the normal ionising voltage.

In general, the current-voltage curves showed the following characteristics: In curves for gradually increasing voltages there was a slight change of slope at about 11·5 volts, the value previously determined by us as the radiation voltage for argon. This was followed by a more marked change of slope at about 15 volts, a value which agrees well with our previous determination of the ionisation voltage. A few volts above this point, the actual voltage differing somewhat in different cases, there occurred a sudden sharp rise in the measured current, the increase being sometimes as much as a hundred times the original current. This rise indicates the increased electron emission already referred to, and was, with very few exceptions, coincident with the first appearance of spectrum lines. On gradually decreasing the applied potential difference a stage was eventually reached at which a correspondingly large decrease in current occurred, but the voltage at which this took place varied over as wide a range as the voltage of disappearance of the "red spectrum" lines. It was found, in fact, to be closely connected with the latter; for although the lines in certain instances ceased to be detectable visually a few tenths of a volt

above the value at which the current fell, yet, on raising the potential difference slightly, lines were detected again provided the fall of the current had not occurred, whereas, if the fall had taken place, the lines could not be made to reappear until the voltage was increased to the value corresponding to the big rise of current in the increasing voltage curve. In view of the fact that, in a very large number of cases, the disappearance of the lines actually coincided with the large decrease of current, it is reasonable to suppose that the apparent discrepancy in the other cases is due to the lines becoming insufficiently intense for visual detection.

The value of the voltage, which was a definite limit for the backing of lines for a considerable range of conditions of pressure and filament temperature, agreed well with the value of the ionising voltage indicated in the curves for increasing voltages. Moreover, in the instances when the lines could be maintained below this limiting value, the decreasing voltage curves show a flattening which commences when this value is passed. These curves thus indicate that a change occurs in the sources of ionisation at this point. Such a flattening of the curve is to be anticipated at the normal ionisation voltage for argon, for below this voltage the production of ionisation by single impacts ceases, and ionisation can only occur by cumulative action. The fact that the spectrum lines of argon could be backed to values of the voltage below the usual limit of 15 volts, only for the larger pressures and for intense bombarding streams, supports the view that its maintenance below 15 volts is due to ionisation by cumulative action.

The continuous curves shown in figs. 2 and 3 illustrate the general characteristics of the current-voltage curves for *increasing* values of the voltage, while the curves drawn with a broken line illustrate the flattening of the curve for *decreasing* voltages when the spectrum lines are maintained by cumulative action (fig. 3), and the absence of such a bend when ionisation by cumulative action does not occur (fig. 2). The curves in fig. 2 represent the results of a series of observations of the variation in the total current between the hot filament and the anode, while the curves of fig. 3 represent the variation of the ionisation current alone. In order to obtain ionisation current curves with the tungsten filament apparatus the following method was used: Between the negative end of the hot filament and the leads of one of the other filaments (cold), a potential difference was applied which was adjusted to be just sufficiently great to prevent electrons from the hot filament from reaching the cold filament. The value of the potential difference necessary for this adjustment was found to be independent of the potential difference applied between the hot filament and the anode. A galvanometer was included in the circuit between the filaments, and observa-

tions of the current were made as the voltage between the hot filament and anode was increased. When ionisation and total current measurements were taken simultaneously, as was sometimes the case, there was no essential difference in the characteristics of the curves obtained. In the two sets of observations represented above the pressure of argon was the same, namely, 0·784 mm., but a much more intense electron stream was employed in the case of the curves of fig. 3 than in those of fig. 2.

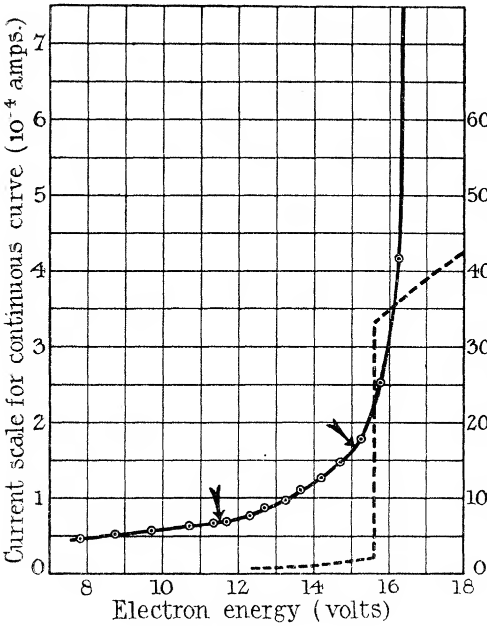

Fig. 2.

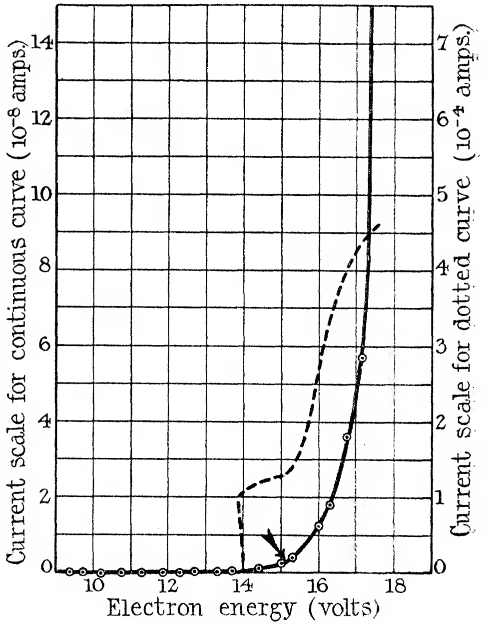

Fig. 3.

The extent to which ionisation was detected below the voltage which corresponds to the normal ionisation of argon, in the curves for gradually increasing values of the voltage, varied very much in different experiments. That the effect detected was really ionisation, and not simply a photoelectric effect of radiation on the negatively charged electrode, was suggested by the fact that the bend is as apparent in the total current curves as in the ionisation curves. It is inconceivable that a current due to a photoelectric emission of electrons, resulting from the radiation produced by the collisions of the primary electrons with gas atoms, could be comparable with the current due to the primary electrons themselves, whereas such an occurrence is readily accounted for if positive ions are produced, since the presence of these gives rise to an increase in the current due to the primary emission itself. That the view is justified was shown in two ways: Firstly, by using the platinum sphere instead of the cold filament as the electrode from which photoelectric

emission could occur. It was found that the magnitude of the effect was unchanged by this alteration. Secondly, in a circuit between the hot filament and one of the cold filaments, the potential difference was so adjusted as to allow a small electron current from the hot filament to pass to the cold filament when a potential difference, which could be varied, was applied between the hot filament and the platinum sphere. It was found that an increase in the electron current to the cold filament occurred simultaneously with the bend in the total current-voltage curve, thus indicating that an increase in the emission from the hot filament had occurred, which could only be brought about by the presence of positive ions.

The cause of the first bend in total current curves and in ionisation current curves must thus be either ionisation of impurity or ionisation of the argon by cumulative action. That the latter is, at any rate, not the main factor is well illustrated by the curves already given in fig. 2, for the curve for increasing voltages shows the 11·5 volts bend quite clearly, whereas the curve for decreasing voltages indicates, according to the reasoning given earlier, that ionisation of argon by cumulative action was not occurring to any extent in this case, even with the increased intensity of the bombarding electron stream which results from neutralisation of the space charge. Hence it appears that the ionisation detected below the normal ionising value in curves for increasing voltages is mainly ionisation of impurity.

Other evidence which points to this conclusion is that the bend was found to be more marked when observations were taken in argon which had been in the apparatus for some time, and in which the filament had been hot for a long period, than when observations were made with argon streaming through the apparatus after submitting the latter to a prolonged pumping. This indicates, moreover, that the impurity arises in the apparatus itself, and is not admitted with the argon. The amount of impurity present must always have been very small, on account of the long continued outgassing to which the apparatus had been subjected, and to the fact that the argon in the apparatus was frequently changed, even when it was not continuously streaming through during the experiments. The only impurity lines which were seen in the spectrum of the luminosity were the H_α and H_β lines, which were visible on some occasions, and a few lines whose wave-lengths agreed with those of certain of the brightest lines of the tungsten arc spectrum. These latter lines were only observed with very brilliant discharges when currents of about 0·5 ampere were passing through the tube. It must be borne in mind, however, that the spectroscopic test for impurities in argon is not one of extreme delicacy. On some occasions, especially with the apparatus of fig. 1, it was thought that traces of bands

could be seen in the spectrum when the conditions were such that the argon lines were only faintly visible. It seemed possible that these might be the carbon oxide spectrum, but the appearance was so extremely faint that we could not be certain from visual observations, and we were unable to obtain a photographic record of the presence of bands even with 8 hours' exposure.

With a very small amount of impurity present in the argon, it would not be expected that sufficient ionisation of it, by direct electron impact, to give an indication in the measured currents would take place; but if this impurity is ionisable by the argon radiation, an indication of ionisation might be expected when this radiation is produced.* Thus the value of the voltage at which ionisation is detected in the increasing voltage curves should be the minimum value for the production of resonance radiation from argon. The value of the resonance voltage deduced in this manner (11·5 volts, fig. 2) agreed with that found in our previous determinations.

When the pressure of the argon was of the order of 1 mm., and when the electron bombardment was intense, ionisation of the gas by cumulative effects took place, probably as the result of electron impacts on argon atoms which were in an abnormal state owing to the absorption of resonance radiation from neighbouring atoms. With the filament as hot as it was safe to make it, the voltage across the discharge tube could be reduced below the minimum radiation voltage for argon without the "red spectrum" lines disappearing. This effect is similar to that obtained by one of the writers with helium,† and is presumably to be explained by the frequency of electron collisions with argon atoms being so great that, on recombination occurring, the returning electron is unable to fall right back to the normal orbit before being again ejected by another impact. It would be expected that the lowest voltage at which all the lines of the red spectrum (excluding those in the extreme ultra-violet) could be maintained would be the minimum voltage required to ionise an atom which has absorbed resonance radiation, *i.e.*, 15·1 volts − 11·5 volts = 3·6 volts. The lowest value to which the voltage could be backed in the present experiments was 6·5 volts, but it must be borne in mind that there are two factors which tend to make the ionisation diminish very rapidly as the minimum value of the electron energy which can produce it—3·6 volts—is approached, viz.:—(*a*) the decreasing efficiency of the electrons in producing ionisation as their energy approaches the critical value; (*b*) the increased proportion of recombination which occurs between positive ions and electrons as the intensity of the electric field is reduced. Owing to both these causes, the number of positive

* F. Horton and D. Bailey, 'Phil. Mag.,' vol. 40, p. 440 (1920).

† *Loc. cit.*

ions reaching the neighbourhood of the filament diminishes until an effective neutralisation of the space charge is no longer maintained. When this stage is reached the electron current across the tube decreases abruptly, and the electron bombardment is then not sufficiently intense to prevent the reversion of the abnormal atoms to the normal condition, so that ionisation ceases.

A striking series of changes in the luminosity of the "red spectrum" lines was observed when the voltage across the tube was gradually reduced from about 25 volts. To begin with, the brightness gradually diminished, but following this there was a noticeable *increase* in the intensity of most of the bright lines as the voltage fell from about 19 volts to about 16 volts, after which the lines diminished in intensity, and finally disappeared. The bright lines λ 7067·5 and λ 6965·8 in the red were not among those whose intensity varied in this way, for they seemed to decrease continuously in brightness as the voltage was lowered. The enhancement with decreasing voltage between 19 and 16 volts was particularly striking in the cases of the lines λ 4510·9, λ 4345·3, λ 4272·3, and lines farther in the blue and violet.

Another point in connection with the behaviour of different lines in the red spectrum under different conditions is worth recording. For small intensities of electron bombardment, the lines in the red and orange parts of the spectrum were only faintly visible even when the lines in the blue were fairly bright. As the current heating the filament was increased, the lines in the red, orange, yellow and green regions increased in brightness far more than the blue and violet lines, and many more lines became visible in these regions. This brightening was particularly striking in the case of the lines λ 7067·5 and λ 6965·8, which were the brightest lines in the red for intense electron emissions, but which for smaller values of the electron emission were hardly visible even when other red lines could be seen clearly.

In general the voltage at which the luminosity first appeared was between 17 volts and 18 volts, but it was found that when a magnetic field was used with the apparatus of fig. 1 the minimum voltage at which a bright luminosity* was produced was 20 volts or more. This delaying of the production of a bright glow in the gas until a higher potential difference had been established is probably due to the concentration of the electron stream into a narrow beam, which increased the chance of the recombination of positive ions and electrons when ionisation of the gas took place, and so

* In some cases with the apparatus shown in fig. 1 a very faint glow was seen at a lower voltage than that at which the sudden large increase of current occurred, and at which the bright glow appeared. This faint glow was presumably due to the recombination which took place before neutralisation of the space charge was effected.

delayed the stage at which positive ions reached the neighbourhood of the filament in sufficient numbers to produce an effective neutralisation of the space charge.

Although about 17 volts was, in general, the lowest voltage at which luminosity was seen when the energy of the electron stream was raised gradually, it was found that if the filament were maintained very hot and *suddenly* the potential difference was switched on, the luminosity would appear (with pressures greater than about 1 mm.) at considerably lower voltages. The lowest voltage at which this effect was obtained was 12·5 volts, the reading of the voltmeter in the presence of the glow being several volts lower than this. When the arc strikes in this way, at a voltage only slightly higher than the minimum radiation voltage, the ionisation of the gas is produced by cumulative effects and positive ions are formed from the start in sufficient numbers to prevent the limitation of the electron current by the mutual repulsion of the emitted electrons, whereas when the voltage is increased gradually this limitation of the electron current is effected before ionisation is produced.

Multiple Ionisation and the Blue Spectrum.

In general the lines of the blue spectrum of argon were not present in the spectrum of the luminosity when it first appeared, but required for their stimulation a higher potential difference across the tube. This is to be expected on the view that these lines result from the recombination of electrons with argon atoms from which two or more electrons have been removed. As the voltage was gradually raised these lines did not appear suddenly, as was usually the case with the "red spectrum" lines, but they were very faint at first and brightened fairly rapidly as the voltage was further increased. The lowest voltage at which they were seen, for increasing values of the voltage, depended to a certain extent upon the intensity of the electron stream, and increased as that intensity was diminished.

Two limiting values of the voltage at which any lines of the blue spectrum could be detected by visual observations were obtained under different conditions. The greater of these, which if Stark's view is correct must be the minimum voltage necessary for the simultaneous removal of two electrons from an argon atom, was about 34 volts, while the lower one, which it would follow is the minimum voltage necessary for the removal of a second electron from an already ionised argon atom, was about 19 volts. It was difficult to fix the upper limit with certainty by visual observations because of the gradual manner of the appearance and disappearance of the "blue spectrum" lines. Moreover, it was impracticable to increase the visibility of the lines at voltages slightly above the limit, by raising the temperature of the filament

because, except at the lowest pressures (*e.g.*, 0·001 mm.) this usually resulted in the production of multiple ionisation by cumulative effects. The limiting values of the voltage for the production of lines of the blue spectrum were therefore investigated photographically, giving long exposures so as to make the detection of lines of feeble intensity more probable. The current-voltage relations were also investigated with a view to determining the voltage at which double ionisation of the argon atom occurred, so as to test the view, already referred to, of the connection between the blue spectrum and multiple ionisation of the atom.

The photographic method of investigation consisted in taking series of photographs of the spectrum of the luminosity at different voltages at intervals of 1 or 2 volts, keeping the total current through the tube constant at all the voltages throughout a series, and examining the plates for the presence of any lines belonging to the blue spectrum only. Among the lines of the blue spectrum which were the first to become visible as the voltage was increased were λ 4430·4 and λ 4426·2, and these lines and others are distinctly visible on all the plates taken with fairly intense electron streams for voltages higher than 19. On the plate taken at 19 volts these two lines can just be detected but they are extremely faint, and at 18·5 volts they are not present at all. A comparison of the plates at different voltages shows that the intensity of the "blue spectrum" lines increased as the voltage was raised from 19 volts to about 24 volts, after which it did not increase further until the voltage reached 34. From 34 volts up to 42 volts the "blue spectrum" lines increased very much in intensity and became more prominent than the lines of the red spectrum. The increase of intensity was first noticeable on the plate at 34 volts. In order to keep the current across the tube the same at all the voltages in a series, it was necessary to reduce the intensity of the electron stream as the voltage was raised. The change in the intensity of the "blue spectrum" lines after 34 volts must, therefore, have been due to the increase in the electron energy and not to an increased intensity of bombardment. Hence the results of the photographic investigation confirm the results of the visual spectroscopic observations and show that there are two limiting voltages associated with the production of "blue spectrum" lines, namely, 19 volts and 34 volts.

The curves given in figs. 4 and 5 illustrate the results obtained in the investigation of current-voltage relations at voltages greater than the normal ionising voltage. The results represented by fig. 4 were taken in argon at a pressure of 0·75 mm., and with the anode 7 mm. from the glowing filament. The curve shows a distinct break at 30 volts. Fig. 5, on the other hand, expresses the results obtained at a pressure of 0·024 mm., and with the anode

and filament only 2 mm. apart. This curve is rather different in form from that of fig. 4, for the current continues to increase considerably with increasing voltage for a much bigger range than in the latter case. There is no indication of a break at 30 volts, but a distinct break occurs at about 34 volts. This difference in the curves is accounted for by the different value of the mean free path of the electrons in the two cases. In the circumstances of fig. 4 each electron would make several collisions between the filament and the anode, so that a bend would be expected to occur in the curve at twice the normal ionising voltage. In the case of fig. 5, the mean free path of the electrons was larger than the distance between the electrodes, so that very few of the electrons were likely to collide twice before reaching the anode. A bend in the curve at twice the normal ionising voltage would therefore not be expected in this curve. Hence it is reasonable to suppose that the bend at 30 volts in the curve of fig. 4 is due to a considerable proportion of the electrons in the stream twice producing single ionisation, while the bend in the curve at 34 volts in fig. 5 is due to the production of doubly ionised argon atoms by the simultaneous removal of two electrons from the normal atom.

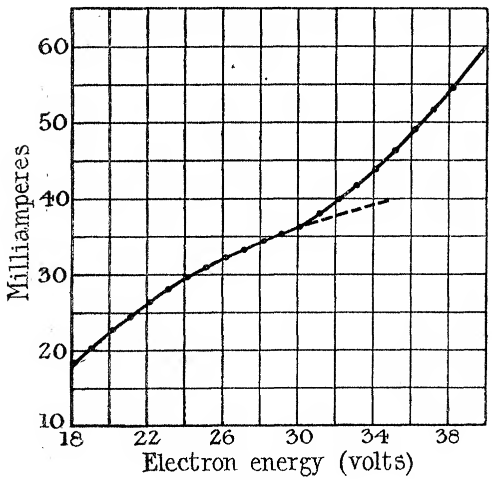

FIG. 4.

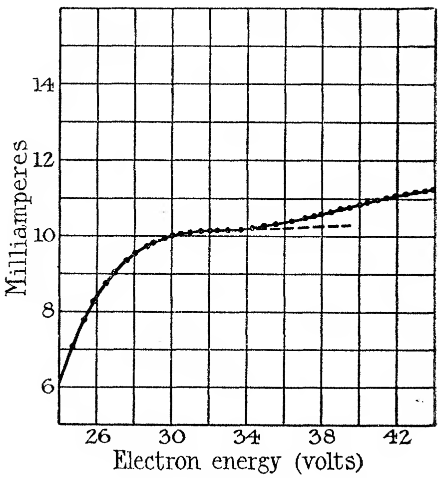

FIG. 5.

The position of the bend in the curve of fig. 4 thus confirms the value of the normal ionising voltage determined by other methods, while the fact that the value of the double ionisation voltage obtained from curves such as that of fig. 5 agrees, within the limits of experimental error, with the greater of the two limits for the appearance of lines of the blue spectrum supports the view that some of these lines result from the recombination of doubly

ionised argon atoms and electrons. The difference between the double ionisation voltage and the normal ionising voltage must be equal to the voltage which is necessary for the removal of a second electron from an already ionised atom, *i.e.* (34 volts − 15 volts =) 19 volts, must be the minimum voltage at which two electrons can be removed from an argon atom by two electron collisions. This value agrees with the lower of the two limits obtained in connection with the appearance of "blue spectrum" lines, and hence supports the view that some of the lines of this spectrum are associated with the presence of argon atoms carrying two positive charges.

When exceedingly intense bombarding electron streams were employed the lines of the blue spectrum, like those of the red spectrum, could be detected at voltages considerably below the usual limits associated with their production. For example, in the instances when the "red spectrum" lines appeared as the voltage was raised to 13 volts or 14 volts, the "blue spectrum" lines were plainly detected in the first flash of the luminosity, but since the potential difference across the tube always fell several volts when the glow appeared, the "blue spectrum" lines did not generally remain; they were visible for an instant only, and were then not seen until the voltage was raised. The lowest voltage at which they were detected on raising the potential difference was 11 volts.

As a result of his experiments on canal rays in argon, Stark has concluded that the blue spectrum of this gas includes radiations which are associated with the presence of trebly charged argon atoms, as well as radiations associated with doubly charged atoms. This suggests that different lines of the blue spectrum require different voltages for their production by electron bombardment. The series of photographs were therefore examined carefully, with a view to ascertaining which lines were associated with atoms having more than two charges. The positions of most of the brighter lines of the blue spectrum, between λ 4888·9 and λ 4014·0, given in the Tables in Kayser's "Handbuch der Spectroscopie," were ascertained from one of the photographs taken at about 46 volts, and the intensity of each line on a series of plates was then investigated. Tables I and II, given below, illustrate the results obtained in the cases of the lines which Stark has classified as "bivalent" and "trivalent" respectively, while Table III gives the results of the investigation of several "blue spectrum" lines between λ 4888·9 and λ 4014·0 which are not classified by Stark.

In each Table a rough estimate of the intensity of the lines at different voltages is given. The presence of any of these lines below 34 volts (the limit at which the simultaneous removal of two electrons by a single collision can occur) is to be attributed to the occurrence of multiple ionisation by

cumulative effects. The increased brightness of many of the lines when the voltage was raised beyond 34 volts is illustrated by the numbers given.

It will be seen from the Tables that there are considerable differences in the minimum voltages at which different " blue spectrum " lines were detected, and that so far as any classification of the lines can be made on the basis of the minimum voltage necessary for their production, this classification does not agree with that given by Stark. It would appear that of the lines classified by Stark, those requiring most energy for their production are λλ 4202·1, 4082·6, 4076·9, 4043·0 and 4014·0, and that these are the " trivalent lines " or, alternatively, that all the lines requiring 38 volts or more for their production are " trivalent," in which case this class includes most of the lines classified by Stark as " bivalent." It must, however, be remarked that if 38 volts is sufficient to produce trebly charged positive ions, these must result from collisions with already ionised argon atoms, for it is exceedingly unlikely that the energy necessary to remove three electrons from a normal argon atom is only 4 volts in excess of that required to remove two

Table I.—Stark's " Bivalent " Lines.

Wave-length.	Intensities.—Electron Energy (volts).										
	42.	40.	38.	36.	34.	32.	30.	28.	26.	24.	20.
4309·3	3	1	0·5	—	—	—	—	0·5	0·5	0·5	—
4300·8	1	0·5	0·5	—	—	—	—	—	—	—	—
4283·0	3	1	0·5	—	—	—	—	—	—	—	—
4277·7	8	6	5	2	2	2	2	2	2	2	—
4237·3	3	1	0·5	—	—	—	—	—	—	—	—
4228·7	8	5	4	1	0·5	0·5	0·5	0·5	0·5	0·5	0·5
4202·1	—	—	—	—	—	—	—	—	—	—	—
4132·0	3	3	2	—	—	—	—	—	1	2	—
4082·6	—	—	—	—	—	—	—	—	—	—	—
4072·2	3	2	1	—	—	—	—	—	—	—	—
4043·0	—	—	—	—	—	—	—	—	—	—	—
4014·0	—	—	—	—	—	—	—	—	—	—	—

Table II.—Stark's " Trivalent " Lines.

Wave-length.	Intensities.—Electron Energy (volts).							
	42.	40.	38.	36.	34.	32.	30.	28.
4434·1	3	1	0·5	0·5	0·5	0·5	—	0·5
4222·8	2	1	—	—	—	—	—	—
4218·8	2	1	—	—	—	—	—	—
4156·3	1	0·5	—	—	—	—	—	—
4104·1	4	3	2	1	1	0·5	0·5	0·5
4076·9	—	— —	—	—	—	—	—	—

Table III.—Other "Blue Spectrum" Lines.

Wave-length.	Intensities.—Electron Energy (volts).												
	42.	40.	38.	36.	34.	32.	30.	28.	26.	24.	20.	19.	18·5.
4888·9	2	1	1	1	1	—	—	—	—	—	—	—	—
4866·1	0·5	—	0·5	—	—	—	—	—	—	—	—	—	—
4847·9	3	2	2	1	0·5	—	—	—	—	—	—	—	—
4806·2	6	3	3	3	2	1	0·5	1	0·5	0·5	0·5	—	—
4765·0	6	3	4	3	1	0·5	0·5	0·5	0·5	0·5	—	—	—
4736·0	5	3	3	2	1	0·5	0·5	0·5	0·5	0·5	—	—	—
4727·0	5	3	4	2	1	0·5	0·5	0·5	0·5	0·5	—	—	—
4658·0	7	4	4	3	1	0·5	0·5	—	—	—	—	—	—
4637·4	2	1	0·5	—	—	—	—	—	—	—	—	—	—
4609·7	7	4	4	3	1	1	1	2	1	1	—	—	—
4590·1	6	4	3	2	1	0·5	0·5	0·5	0·5	0·5	—	—	—
4579·5	6	4	4	3	1	0·5	0·5	0·5	0·5	0·5	0·5	—	—
4545·3	6	5	5	4	2	0·5	0·5	1	0·5	1	0·5	—	—
4503·2	1	0·5	—	—	—	—	—	—	—	—	—	—	—
4498·7	1	—	—	—	—	—	—	—	—	—	—	—	—
4491·2	1	1	0·5	—	—	—	—	—	—	—	—	—	—
4488·4	—	—	—	—	—	—	—	—	—	—	—	—	—
4482·0	8	7	5	3	1	1	1	2	0·5	1	—	—	—
4431·2	3	3	3	2	1	—	—	—	—	—	—	—	—
4430·4	8	7	6	4	3	1	1	2	1	2	1	0·5	—
4426·2	10	10	10	8	5	2	2	3	2	3	2	0·5	—
4401·2	8	7	7	6	4	2	2	2	2	2	1	0·5	—
4400·3	5	4	3	3	1	0·5	—	—	—	—	—	—	—
4379·8	7	7	7	5	3	1	2	2	2	2	1	—	—
4371·5	—	—	—	—	—	—	—	—	—	—	—	—	—
4370·9	8	8	7	5	3	1	2	2	2	2	1	—	—
4362·2	3	2	1	—	—	—	—	—	—	—	—	—	—
4352·4	5	4	4	3	1	—	—	0·5	—	—	—	—	—
4348·1	10	10	10	10	8	5	4	5	3	4	3	0·5	0·5
4332·2	1	1	1	—	—	—	—	—	—	—	—	—	—
4331·3	1	0·5	0·5	—	—	—	—	—	—	—	—	—	—

electrons simultaneously from such an atom, namely, 34 volts. The significance to be attached to 38 volts as a critical electron energy—if this voltage is a genuine limit for the production of trebly ionised atoms by cumulative effects—is doubtful, because of the various possible ways in which the energy necessary for the removal of three electrons might be acquired from the combined effects of two or three electron collisions.

Conclusion.

If the square roots of the voltages connected by the quantum relation with the frequencies of the various K X-ray absorption limits are plotted against the corresponding atomic numbers, it is found that the square root of the accepted value of the ionisation voltage of helium falls on the curve at the point corresponding to atomic number 2. This fact has been interpreted as indicating that the ionisation voltage of helium corresponds to the K X-ray absorption limit of this element. A similar relation has been shown by

Mohler and Foote* to hold in the case of the ionisation voltage of neon (16·7 volts)† and the L absorption limits. It might, therefore, be anticipated that in the case of argon a similar connection would hold for its ionisation voltage and the voltages corresponding to one of the M absorption limits of other elements. Except in the case of the elements of high atomic number, however, very little information with regard to M absorption limits is available. In the cases of the elements molybdenum (atomic number 42), copper (atomic number 29), and potassium (atomic number 19) determinations of the voltages corresponding to the M radiations have recently been made.

Richardson and Bazzoni‡ found that, in the case of molybdenum, soft X-rays were produced when the applied voltage was about 356 volts, and they classified the radiation they obtained as belonging to the M series. In fig. 6, the square roots of the voltages connected by the quantum relation with the frequencies of the M_α, M_β and M_γ lines are plotted against the corresponding atomic numbers for the elements for which M X-ray data are available.§ It will be seen that the prolongation of the M_γ line passes through the molybdenum point determined by Richardson and Bazzoni. It seems probable that the voltage required to excite M radiations by electron bombardment is that corresponding to the frequency of one of the M absorption limits. Hence it is reasonable to assume that one of the M absorption limits for molybdenum is not far from 356 volts. The curve drawn with a broken line in fig. 6 joins the points obtained by plotting the square root of the voltage corresponding to the frequency of the M absorption limit (ν_{M_a}) against the atomic number (A) for the cases of argon and molybdenum, taking these voltages to be 15·1 and 356 respectively. If the relation $\sqrt{(\nu_{M_a})} = kA + c$ holds between molybdenum and argon, then the value of the voltage corresponding to ν_{M_a} for any element intermediate to these should be obtainable from this line. The value deduced for potassium from this curve is 20·3 volts, which agrees within the limits of experimental error with one of the critical points recently found by Mohler and Foote‖ in the radiation curve for this element. Two breaks were found by these experimenters in the radiation curve, one at 20 ± 1 volts and another more marked break at 23 ± 1 volts. A break at the latter point was also obtained in their ionisation curves. Within the limits of experimental error, the difference between these two voltages agrees with the normal

* F. L. Mohler and P. D. Foote, 'Journal of the Opt. Soc. of America,' vol. 5, p. 328 [1921].

† F. Horton and A. C. Davies, 'Roy. Soc. Proc.,' A, vol. 98, p. 124 (1920).

‡ O. W. Richardson and C. B. Bazzoni, 'Phil. Mag.,' vol. 42, p. 1015 (1921).

§ W. Duane, 'Bulletin of Nat. Research Council,' vol. 1, p. 383 (1920).

‖ F. L. Mohler and P. D. Foote, 'Phys. Rev.,' vol. 18, p. 94 (1921).

ionising voltage of potassium found by these experimenters, viz., 4·3 volts. This fact suggests that the lower of the two voltages given above is the one which really corresponds to the M absorption limit for potassium, and that the greater of the two voltages given above is that required to remove two electrons simultaneously from the potassium atom, the outer more loosely attached electron, and one from the M ring of electrons. On this view, the occurrence of a break in the ionisation curves at 23 ± 1 volts is readily explained, and the agreement between the lower value given above and that determined from the curve of fig. 6 is very satisfactory.

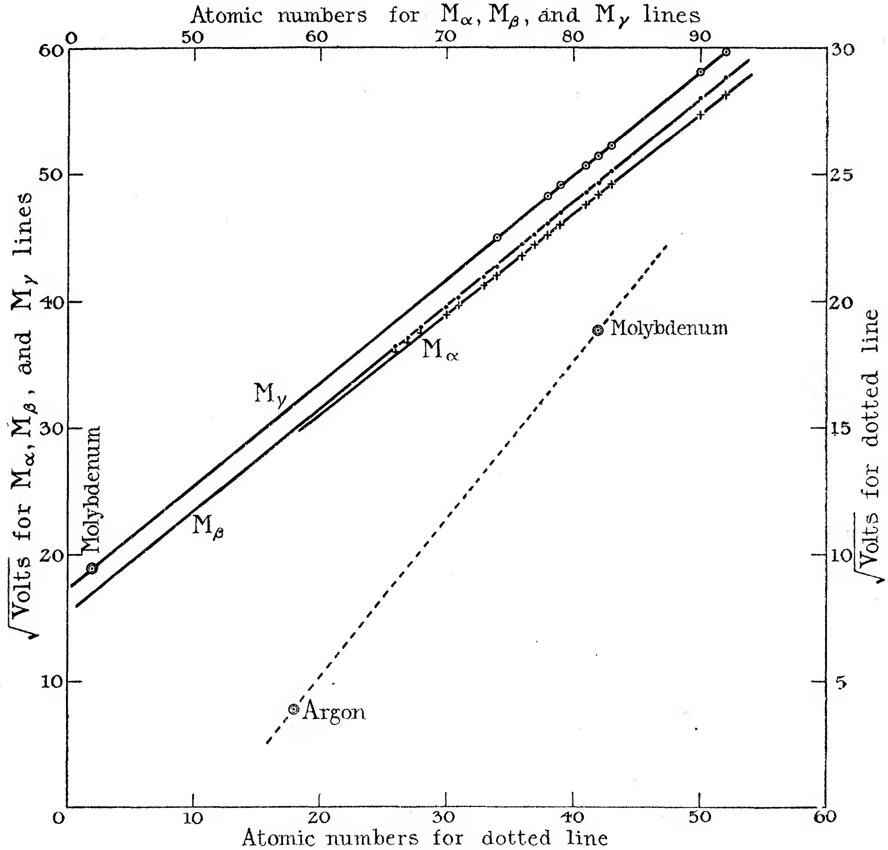

Fig. 6.

In the case of copper, the other element between molybdenum and argon for which M series X-ray data are available, the value of the voltage corresponding to the frequency of the M absorption limit deduced from the curve is about 116 volts. This value agrees within the limits of experimental error with one of the critical points found by Kurth,* but ascribed

* E. H. Kurth, 'Phys. Rev.,' vol. 18, p. 461 (1921).

by him to a hypothetical N series. Kurth obtained another break in his radiation curve for copper, at about 300 volts, and this he attributes to the M series of copper. This value is, of course, very far from falling on the curve connecting Richardson's molybdenum value and our own argon value. Kurth admits, however, that the value attributed by him to an N series may really correspond to an M series.

In the case of iron also, Kurth obtained breaks in the radiation curve, which he attributed to N and M series respectively. Neither of these values, however, fall very near the molybdenum-argon line in fig. 6. Experiments to investigate the voltages necessary for the excitation of the M radiations of other elements in this region are at present in progress in this laboratory.

Summary.

The ionisation of argon by electron collisions has been investigated by spectroscopic observations taken in conjunction with current-voltage curves. The authors' previous determinations of the minimum electron energies for the production of resonance radiation (11·5 volts) and ionisation (15·1 volts) have been confirmed and, in addition, the energy necessary to remove two electrons simultaneously from a normal argon atom has been found to be 34 volts.

It has been found that many lines in the blue spectrum of argon appear simultaneously with the occurrence of double ionisation, but that others need a greater electron energy for their stimulation, and therefore probably require the removal of more than two electrons from the normal atom for their production.

Certain of the lines of the blue spectrum have been classified by Stark as "bivalent" and certain others as "trivalent," but this classification is not confirmed by the results of the determination of the minimum electron energies required for their stimulation.

So far as can be judged from the limited data available, it appears probable that the ionisation voltage (15·1 volts) is related to one of the M X-ray absorption limits of the various elements in a manner analogous to that in which the helium ionisation voltage is related to the K absorption limits and the neon ionisation voltage (16·7 volts) to the L absorption limits. Thus it seems reasonable to suppose that the frequency with which the ionisation voltage of argon is connected by the quantum relation is that of one of the M absorption limits for argon.

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